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Spatial and Seasonal Concentration of Dissolved Nutrients in River Ethiope, Nigeria

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ABSTRACT

This study examined the variation of dissolved nutrients along River Ethiope, Delta State, Nigeria. Water samples were collected at the upper course (Umutu), middle course (Eku) and lower course (Sapele) during early, peak and late periods of the wet and dry seasons. Concentration of Ca^{2+}, Mg^{2+}, K^+, Na^+, NO_3^-, HCO_3^-, Cl^- and SO_4^{2-} were analyzed. Findings reveal insignificant seasonal variations in the concentration of the nutrients at each of the stages and along the course of RE. Positive significant relationships were observed between Na^+ and K^+, SO_4^{2-} and Na^+ ($P < 0.05$) and SO_4^{2-} and K^+ ($P < 0.01$) at the upper course. At the middle course, positive significant relationships existed between NO_3^- and Ca^{2+}, Ca^{2+} and Mg^{2+}($P < 0.05$) and between HCO_3^- and Na^+ ($P < 0.01$) while at the lower course, positive significant relationships were detected between Na^+ and K^+, NO_3^- and Ca^{2+}, HCO_3^- and K^+ as well as between HCO_3^- and Na^+ ($P < 0.05$). At the lower course, positive significant relationships existed between $SO_4^{2-}$and and K^+, Na^+ and HCO_3^-. Highest and lowest concentrations of nutrients at the upper course were Cl^- (81.35±14.17 mg/l) and SO_4^{2-}(0.31±0.11 mg/l) respectively while highest and lowest concentrations at the middle course were Cl^- (81.29±17.86 mg/l) and SO_4^{2-}(0.29±0.09 mg/l) respectively whereas at the lower course, highest and the lowest concentrations were Cl^- (72.63±18.17 mg/l) and NO_3^- (0.12±0.07 mg/l) respectively. The upper course largely witnessed the highest concentration of nutrients. Findings suggest similarities in the natural and anthropogenic sources of some of the nutrients at the catchment area of RE.

1. INTRODUCTION

Rivers plays critical roles in the socio-economic development of societies. Thus, over the years, rivers constitute veritable communication, industrial, and recreational assets and form a major source of domestic water in some climes.

Globally, several water environments have witnessed major increase in nutrients enrichment (Arnell *et al*., 2015). River discharge is a key corridor for nutrients dispersion commencing from the continents to oceans and consequently, leading to pollution of water (Liu *et al*., 2015; Liang and Xian, 2018). Concentration of nutrients reveals unique regular reaction to fluctuating hydrographical flow regimes and biological activities (Cai *et al*., 2008). Wastewater, fertilizers, atmospheric deposition and soil have also been identified as sources of dissolved nutrients in rivers (Gong *et al*., 2015).

Comparatively, river discharge and salinity have been identified as key parameters that influence a variety of environmental conditions that determine bacterial ecology diagonally the river-ocean band (Doherty *et al*., 2017). Thus, as rivers experience fluxes in their regime, nutrient concentration is expected to fluctuate. The hydrology of a river could alter significantly along its watershed due to climate change and water management practices with resultant effects on its nutrients (Gong *et al*., 2015). Enhancement in nutrients supply is a precondition to the activation of eutrophication (Santana *et al*., 2016).

Concentrations of compounds in water are mostly associated with point source pollution (household and industrial wastewater), non-point source contagion (agriculture activities), as well as natural factors such as weathering of soil and rock (Halliday *et al*., 2014; Barakat *et al*., 2016). Thus, while some nutrients-enrichments in rivers are derived from natural sources, nitrogen is widely recognized as mainly originating from anthropogenic (Wen *et al*., 2008). Therefore, water quality is in nature uneven both spatially and over time (Nilsson and Renofalt, 2008).

While nutrients concentration can lead to eutrophication and acidification during period of low flows, nutrients are removed from water course via transport, uptake by riparian plants and denitrification during period of high flows (Nilsson and Renofalt, 2008). Excess nutrients encourage the extreme escalation of algae growth and leading to the growth of a great deal of microcystin in aquatic environment with consequential health danger to humans and severe environmental challenges (Yang *et al*., 2007). Furthermore, contaminated waters, increase concentration of nitrogen, especially in the variety of NH_4^+, NO_2^-, and NO_3^-, are known to be harmful to diverse water organisms and can amount to a human health risk (Rahaman *et al*., 2014). Efficient use of water assets demands information concerning the river water quality and its variation (Barakat *et al*., 2016). It has therefore been advocated that regular monitoring, through periodic testing is key to ascertaining the level of their physical-chemical and biological properties of rivers (Usherhe *et al*., 2016).

Regrettably, earlier studies have not examined variations in dissolved nutrients at the different stages of River Ethiope (RE) viz-a-viz clearly defined seasonal variations. This paper, therefore, presents the findings of the concentration of dissolved nutrients of RE along its course during the early, peak and late spells of the wet and dry seasons.

2. MATERIALS AND METHODS

2.1. Study Area

River Ethiope (RE) (Figure 1) is a prominent freshwater system in Delta State, Nigeria (Ikomi *et al*., 2005; Iloba, 2017). It takes its source from a spring at Umuaja and flows for about 100km before emptying into the Benin River and is relevant for household water, fishing, sand-mining, agriculture, industrial use and transportation (Omo-Irabor and Olobaniyi, 2007; Usherhe *et al*., 2016; Iloba, 2017). The river is permanent and it is fed by groundwater discharges, rainfall together with overland run-off from adjoining areas (Omo-Irabor and Olobaniyi, 2007). The catchment area is made up of Akata formation which consists of basal units composed majorly of marine shale, depositional sequence of paralic Agbada formation and the Benin

Formation which constitutes the topmost components made up of fluviatile gravels and sand layers (Omo-Irabor and Olobaniyi, 2007). The wet season within the river catchment area lasts from mid-March to October and annual rainfall amount is usually above 2000 mm. RE flows within the rainforest, especially at the upper and middle stages while the lower course predominantly falls within freshwater swamps.

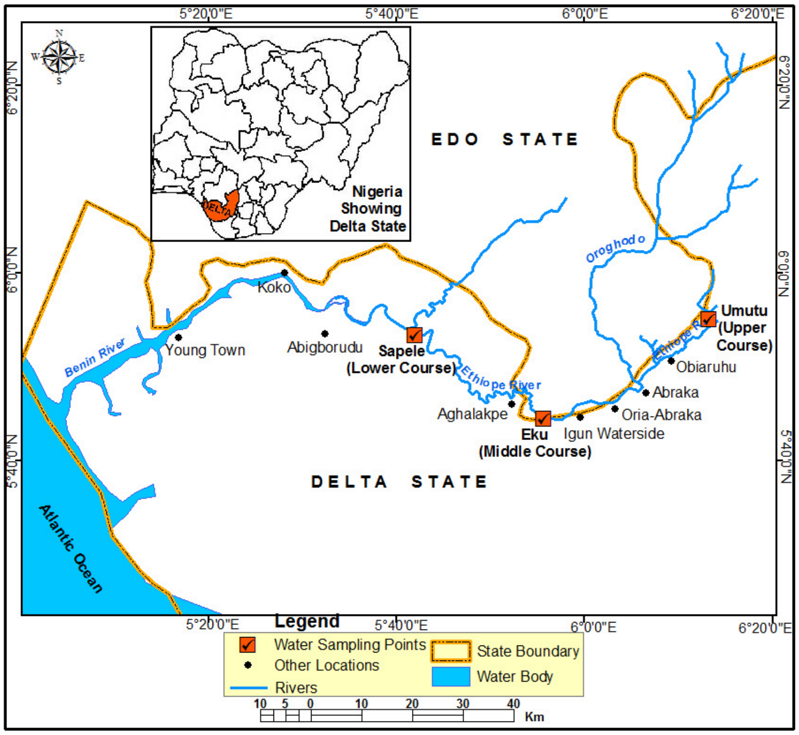

Figure 1: Sampling points along the course of River Ethiope (Open Street Map Database 2019)

2.2. Sample Collection

Water samples were collected at three locations along the course of River Ethiope (RE) during 2018/2019. The three locations were: Umutu (upper course), Eku (middle course) and Sapele (lower course). The water samples were collected in the wet and dry seasons. The two seasons were segmented into early, peak and late time frames. Two water samples were collected during each of the seasonal segments fortnightly. Thus, 36 water samples were collected at the Umutu, Eku and Sapele during the early dry season (November), peak dry season (February), peak dry season (March), early rainy season (April), peak rainy season (September) and late rainy (October). The water samples were labeled and taken to the laboratory and the concentration of Ca^{2+} (Calcium ion), Mg^{2+} (Magnesium ion), K^{+} (Potassium ion), Na^{+} (Sodium ion), NO_3^- (Dioxonitrate III ion), HCO_3^- (Hydrogentrioxocarbonate IV ion), Cl^- (Chloride ion) and SO_4^{2-} (Tetraoxosulphate VI ion).

2.3. Laboratory Analysis

Based on the Brucine method for the determination of nitrate, 10 ml of the sample was transferred into a 50 ml volumetric flask and 2 ml of brucine reagent was added which was immediately followed by addition of 10 ml of tetraoxosulphate IV acid (EPA, 1971). The combination was stirred and was allowed to stand for

10 minutes. The volumetric flask was air cooled for 15 minutes and was adjusted up to 50 ml mark. The set of working standards and the blank were similarly handled. The absorbance was measured at 470 nm with UV Spectrophotometer. Dioxonitrate III ion (mg/l) was computed as instrument reading x slope reciprocal x colour volume x extra volume/ volume of sample used.

The procedure for the determination of sulphate commenced with the transfer of 10 ml of the sample into 50 ml of volumetric flask. This was followed by addition of distilled water to adjust the volume to 20 ml and 1 ml of barium chloride (gelatine reagent) was added and adjusted to the volume with distilled water. The mixture was stirred thoroughly and left to set for 30minutes. The standards and the blank were treated alike. The absorbance of the solution was read at 420 nm in a UV spectrophotometer. Tetraoxosulphate VI ion (mg/l) was calculated as instrument reading x slope reciprocal x colour volume x extra volume/ volume of sample used. Determination of K^+, Na^+, Ca^{2+} and Mg^{2+} were by use of flame photometer (APHA, 1998). Sample was sprayed into a gas flame and was excited under a carefully controlled and reproducible condition. The desired spectra line was isolated by the use of interference filter. The intensity of light was measured by phototube potentiometer. The intensity of light at 768 nm is proportional to the concentration of potassium in the sample.

Mohr's method which is based on silver nitrate titration was used to determine chloride concentration (Shuklia and Arya, 2018). Based on this method, 5 ml of the sample was taken and few drops of K_2CrO_4 solution was added and titrated with standard silver nitrate ($AgNO_3$) to a pinkish endpoint. Similarly, blank value was determined by titrating 5 ml of distilled water with standard silver nitrate ($AgNO_3$) with few drops of K_2CrO_4 indicator.

2.4. Statistical Analysis

The variations of the concentration of the selected dissolved nutrients were analyzed using mean, standard deviation, student's *t* test and analysis of variance (ANOVA). Student's *t* test was used to examine the significances of the difference in the concentration of the selected dissolved nutrient between the wet and dry seasons. ANOVA was employed to ascertain the significance of the variation of the concentration of the selected dissolved nutrients among early, peak and late seasons of the wet and dry season and among the three stages of the river. Pearson product moment correlation was used to examine the relationship between the nutrients.

3. RESULTS AND DISCUSSION

The concentrations of the selected dissolved nutrients at the upper course (Umutu), during the sampling seasons are presented in Table 1. Generally, the concentration of the nutrients did not depict a clear seasonal pattern. Chloride ion exhibited the highest concentration during the sampling seasons while NO_3^- and SO_4^{2-} appeared to have lowest concentration. Chloride ion exhibited the highest inter-seasonal variation while NO_3^- varied least inter-seasonally. The concentration of Ca^{2+} was highest in the peak of the dry season and lowest in the peak of the rainy season while the mean for the seasons was 3.93±0.33 mg/l. The mean of the concentrations of Mg^{2+} during the sampling period was 4.07±0.32 mg/l with the highest and lowest concentrations occurring in the peak of the dry season and late dry seasons at 4.48 mg/l and 373 mg/l respectively. The mean of the concentrations of K^+ was 2.51±0.76 mg/l. The concentrations of K^+ were highest (3.48 mg/l) and lowest of (1.56 mg/l) and were observed in the peak of the rainy season and peak of the dry seasons respectively. The mean concentration of dissolved Na^+ for all the seasons was 2.49±1.04

mg/l. The highest and lowest concentrations of Na^{+} were observed in early rainy season and peak dry season at 3.87 mg/l and 0.81 mg/l respectively. Concentration of NO_3^{-} was highest and lowest in peak dry season and early rainy season at 0.39 mg/l and 0.27 mg/l respectively. While the mean value of NO_3^{-} was 0.33±0.05 mg/l. The concentrations of HCO_3^{-} was highest at 3.48 mg/l in early dry season while it was lowest at 2.05 mg/l early dry season. The mean concentration of HCO_3^{-} for the seasons was 2.73±0.52 mg/l. Concentrations of dissolved Cl^{-} was highest in late dry season at 96.74 mg/l and lowest in the early rainy season at 65.68 mg/l. Mean concentration of Cl^{-} was 81.35±14.17 mg/l. Dissolved SO_4^{2-} was highest in early rainy season and peak of the rainy season each at 0.40 mg/l while it was lowest in peak dry season at 0.14 mg/l. The mean value of dissolved SO_4^{2-} for the seasons was 0.31±0.11 mg/l.

Table 1: Seasonal variation of dissolved nutrients at the upper course (Umutu) of RE

Nutrients (mg/l)	Early rainy season	Peak rainy season	Late rainy season	Early dry season	Peak dry season	Late dry season	$\bar{X} \pm SD$
Ca^{2+}	3.97	3.31	3.93	4.12	4.28	3.95	3.93 ± 0.33
Mg^{2+}	3.85	4.01	4.45	3.93	4.48	3.73	4.07 ± 0.32
K^{+}	3.12	3.48	2.87	1.91	1.56	2.11	2.51 ± 0.76
Na^{+}	3.87	3.14	2.44	2.01	0.81	2.71	2.49 ± 1.04
NO_3^{-}	0.27	0.30	0.31	0.38	0.39	0.33	0.33 ± 0.05
HCO_3^{-}	3.48	2.60	3.10	2.05	2.80	2.35	2.73 ± 0.52
Cl^{-}	65.68	94.96	70.11	70.11	90.52	96.74	81.35 ± 14.17
SO_4^{2-}	0.40	0.40	0.39	0.25	0.14	0.30	0.31 ± 0.11

The result of ANOVA of inter-seasonal variation of the dissolved nutrients at the upper course of RE is presented in Table 2. The analysis shows that the concentration of the dissolved nutrients insignificantly varied inter-seasonally at the upper course of RE.

Table 2: ANOVA of the inter-seasonal variation of dissolved nutrients at the upper course (Umutu) of RE

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Between groups	114.27	5	22.85	0.03	1.00	2.44
Within groups	33760.61	42	803.82			
Total	33874.88	47				

The correlations coefficients between the nutrients at the upper course of RE are presented Table 3. Positive significant relationships existed between Na^{+} and K^{+}, SO_4^{2-} and Na^{+} ($P < 0.05$) and SO_4^{2-} and K^{+} ($P < 0.01$). On the contrary, negative significant relationships exist between K^{+} and Ca^{2+}, NO_3^{-} and K^{+}, NO_3^{-} and K^{+} (P < 0.05) as well as NO_3^{-} and Na^{+} and SO_4^{2-} and NO_3^{-} ($P < 0.01$).

Table 3: Correlation coefficients of between nutrients at the upper course (Umutu) of RE

Nutrients	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	NO_3^{-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}
Ca^{2+}	1							
Mg^{2+}	.266	1						
K^{+}	-.826*	-.188	1					
Na^{+}	-.594	-.642	.824*	1				
NO_3^{-}	.603	.337	-.901*	-.925**	1			
HCO_3^{-}	-.002	.290	.491	.394	-.648	1		
Cl^{-}	-.328	-.069	-.159	-.255	.224	-.417	1	
SO_4^{2-}	-.711	-.318	.937**	.897*	-.930**	.436	-.285	1

*Correlation is significant at 0.05 level (2-tailed); **Correlation is significant at 0.05 level (2-tailed)

The seasonal variations of dissolved nutrients at the middle course (Abraka) of RE are presented in Table 4. Calcium ion concentration was highest in the peak of the dry season while it was lowest in the peak of the rainy season at 4.08 mg/l and 2.36 mg/l respectively with a mean 3.39±0.67 mg/l. Like Ca^{2+}, Mg^{2+} concentrations were highest and lowest in the peaks of the dry season and rainy season at 3.47 mg/l and 3.10 mg/l respectively. However, the mean of Mg^{2+} at the middle course was 3.27±0.17 mg/l. Unlike Ca^{2+} and Mg^{2+}, K^+ concentrations were highest and lowest during the peak of the rainy season and peak of the dry season at 3.25 mg/l and 1.42 mg/l respectively. At the middle course, K^+ had a mean of 2.40±0.69 mg/l. Sodium ion witnessed the highest and lowest concentrations in the early rainy season and early dry season at 2.96 mg/l and 1.42 mg/l respectively while the mean was 2.40±0.73 mg/l. Early dry season and peaky dry season equally recorded the highest concentration of NO_3^- at 0.36 mg/l while the lowest concentration was recorded in early rainy season at 0.27mg/l with a mean of 0.31±0.04 mg/l. Concentration of HCO_3^- was highest and lowest in early rainy season and peak dry season at 3.41 mg/l and 1.95 mg/l respectively while the mean was 2.53±0.50 mg/l. The highest and lowest concentrations of Cl^- were in the peak of the dry season and late rainy season at 111.82 mg/l and 64.79 mg/l while the mean was 81.29±17.86 mg/l. Concentrations of SO_4^{2-} were highest and lowest in the peak of the rainy season and peak dry season respectively at 0.40 mg/l and 0.15 mg/l respectively while the mean was 0.28±0.09 mg/l. The relatively high concentration of Cl^- during the peak of the dry season could be ascribed to higher evaporation coupled with low discharge.

Table 4: Seasonal variation of dissolved nutrients at the middle course (Eku) of RE

Nutrients (Mg/l)	Early rainy season	Peak rainy season	Late rainy season	Early dry season	Peak dry season	Late dry season	$\bar{X} \pm SD$
Ca^{2+}	3.03	2.36	3.39	4.08	4.13	3.39	3.39 ± 0.67
Mg^{2+}	3.18	3.10	3.15	3.49	3.47	3.24	3.27 ± 0.17
K^+	2.96	3.25	2.70	2.05	1.42	2.01	2.40 ± 0.69
Na^+	3.38	2.32	2.48	1.67	1.26	2.22	2.22 ± 0.73
NO_3^-	0.27	0.28	0.31	0.36	0.36	0.31	0.31 ± 0.04
HCO_3^-	3.41	2.55	2.50	2.20	1.95	2.60	2.53 ± 0.50
Cl^-	67.45	90.49	64.79	70.64	111.82	82.54	81.29 ± 17.86
SO_4^{2-}	0.33	0.40	0.37	0.24	0.15	0.28	0.29 ± 0.09

The output of ANOVA of the inter-seasonal variation of the dissolved nutrients at the middle course of RE is presented in Table 5. The analysis shows that there is no significant inter-seasonal variation in the dissolved nutrients at the middle course of RE.

Table 5: ANOVA of dissolved nutrients among different seasons at the middle course (Eku) of RE

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	178.67	5	35.73	0.04	1.00	2.44
Within Groups	34436.92	42	819.93			
Total	34615.59	47				

Table 6 shows the correlation coefficients between the nutrients at the middle course of RE. The analysis reveals positive significant relationships between Mg^{2+} and Ca^{2+}, NO_3^- and Ca^{2+}, NO_3^- and Mg^{2+} ($P < 0.05$) as well as $HCO_3^-$and Na^+ ($P < 0.01$). Contrarily, negative significant relationships occurred between NO_3^- and Mg^{2+}, HCO_3^- and NO_3^-, SO_4^{2-} and Ca^{2+}, SO_4^{2-} and NO_3^- ($P < 0.05$) as well as SO_4^{2-} and Mg^{2+} ($P < 0.01$) at the middle course of RE.

Table 6: Correlation coefficients of between nutrients at the middle course (Eku) of RE

Nutrients	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	HCO_3^-	Cl^-	SO_4^{2-}
Ca^{2+}	1							
Mg^{2+}	.909*	1						
K^+	-.765	-.504	1					
Na^+	-.665	-.763	.070	1				
NO_3^-	.914*	.922**	-.450	-.896*	1			
HCO_3^-	-.604	-.650	.018	.973**	-.858*	1		
Cl^-	.181	.360	.249	-.660	.371	-.579	1	
SO_4^{2-}	-.871*	-.917**	.563	.719	-.827*	.580	-.563	1

*Correlation is significant at 0.05 level (2-tailed); **Correlation is significant at 0.05 level (2-tailed)

The seasonal concentrations of the selected dissolved nutrients at the lower course of RE are presented in Table 7. The data show that Ca^{2+} concentrations were highest and lowest in the peak of the dry season and early rainy season at 3.90 mg/l and 1.65 mg/l respectively with a mean of 2.39±0.90 mg/l. Similarly, Mg^{2+} concentrations were highest and lowest in the peak of the dry season and early rainy season at 2.89 mg/l and 1.40 mg/l respectively with a mean of 2.32±0.55 mg/l. Dissolved K^+ witnessed its highest and lowest concentration in the peak of the rainy season and peak of the dry season at 3.20 mg/l and 1.51 mg/l respectively with a mean of 2.44±0.62 mg/l. Sodium ion appeared to have the highest concentration in the peak of the rainy season at 3.20 mg/l while it dropped to its lowest concentration at 0.49 mg/l in the peak of the dry season with a mean of 2.21±0.97 mg/l. Dioxonitrate III ion was equally most concentrated in the early dry season and peak dry season at 0.33 mg/l while its lowest concentration occurred in early rainy season at 0.16 mg/l with a mean of 0.25±0.07. Hydrogentrioxocarbonate IV ion was most concentrated in the peak of the rainy season at 3.43 mg/l and least concentrated in the peak of the dry season at 1.40 mg/l with a mean of 2.82±0.76 mg/l. As in the upper course and middle course, the concentrations of Cl^- appeared to be relatively higher than that of the other nutrients in all the sampling seasons. The concentration of Cl^- was highest in the peak of the dry season at 99.40 mg/l while its lowest concentration occurred in late rainy season at 53.25 mg/l with a mean of 72.63±18.17 mg/l. The highest and lowest concentrations of SO_4^{2-} occurred in the peak of the rainy season and peak of the dry season at 0.42 mg/l and 0.15 mg/l respectively while the mean was 0.30 ±0.09 mg/l. Comparatively, NO_3^- and SO_4^{2-} appeared to have the lowest concentrations in all the sampling seasons.

Table 7: Seasonal variation of dissolved nutrients at the lower course (Sapele) of RE

Nutrients (Mg/l)	Early rainy season	Peak rainy season	Late rainy season	Early dry season	Peak dry season	Late dry season	$\bar{X} \pm SD$
Ca^{2+}	1.65	1.80	2.16	3.07	3.90	1.76	2.39 ± 0.90
Mg^{2+}	1.40	2.74	2.43	2.48	2.89	1.96	2.32 ± 0.55
K^+	2.86	3.20	2.82	2.13	1.51	2.15	2.44 ± 0.62
Na^+	2.91	3.15	2.41	1.77	0.49	2.56	2.21 ± 0.97
NO_3^-	0.16	0.20	0.23	0.33	0.33	0.25	0.25 ± 0.07
HCO_3^-	3.43	3.40	2.95	3.11	1.40	2.63	2.82 ± 0.76
Cl^-	59.46	78.10	53.25	59.46	99.40	86.09	72.63 ± 18.17
SO_4^{2-}	0.30	0.42	0.36	0.31	0.15	0.27	0.30 ± 0.09

Table 8 shows the ANOVA output of the inter-seasonal variation of the selected dissolved nutrients at the middle course of RE. The analysis reveals that there is no significant inter-seasonal variation in the concentration of the dissolved nutrients at the middle course.

Table 8: ANOVA of dissolved nutrients among different seasons at the lower (Sapele) course of RE

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between groups	188.35	5	37.67	0.06	1.00	2.44
Within groups	27839.24	42	662.84			
Total	28027.6	47				

The correlation coefficients of the nutrients at the lower course of RE are presented in Table 9. Positive significant relationships occurred between Na^+ and K^+, NO_3^- and Ca^{2+}, NO_3^- and K^+, HCO_3^- and K^+, SO_4^2 and K^+, SO_4^2 and Na^+ as well as SO_4^{2-} and HCO_3^- ($P < 0.05$). On the contrary, negative significant relationships were observed between HCO_3^- and Ca^{2+} ($P < 0.05$) as well as between Na^+ and Ca^{2+} ($P < 0.01$)

Table 9: Correlation coefficients of between nutrients at the lower course (Sapele) of RE

Nutrients	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	HCO_3^-	Cl^-	SO_4^{2-}
Ca^{2+}	1							
Mg^{2+}	.661	1						
K^+	-.809	-.313	1					
Na^+	-.968**	-.547	.901*	1				
NO_3^-	.885*	.639	.849*	-.859*	1			
HCO_3^-	-.775	-.496	.862*	.886*	-.678	1		
Cl^-	.414	.412	-.591	-.494	.381	-.753	1	
SO_4^{2-}	-.693	-.084	.912*	.834*	-.586	.868*	-.611	1

**Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed)

The mean seasonal concentrations of the sampled nutrients are presented in Table 10. While concentrations of Ca^{2+}, Mg^{2+}, NO_3^- and Cl where higher in the dry season, K^+, Na^+ HCO_3^- and SO_4^{2-} were higher during the rainy season.

Table 10: Mean seasonal concentrations of dissolved nutrients along the course of RE

Nutrient (mg/l)	Rainy season	Dry season
Ca^{2+}	2.84	3.52
Mg^{2+}	3.14	3.25
K^+	3.03	1.90
Na^+	2.90	1.73
NO_3^-	0.26	0.33
HCO_3^-	3.05	2.39
Cl^-	71.59	83.72
SO_4^{2-}	0.37	0.24

The mean concentrations of the sampled dissolved nutrients at the upper course, middle course and lower course of RE are presented in Table 11. Overall, the upper course of RE witnessed the highest concentration of all but HCO_3^- in the dissolved nutrients investigated in this study. Characteristically, the upper course of a river is predominantly a zone of down-cutting (vertical corrasion). Thus, intensive erosion may have contributed to the relatively accentuated level of the concentrations. The analysis reveals decrease in the concentration of some of the nutrients (Na^+, NO_3^- and Cl^-) from the upper course to the lower course of RE.

Contrastingly, the lowest concentrations of Mg^{2+} and K^{+} and HCO_3^- and SO_4^{2-} were recorded at the middle course. The relatively lower concentrations of some of the nutrients, especially NO_3^- at the lower course suggest self-purification as the river progresses (Bogdal *et al.*, 2016).

Table 11: Mean concentrations of dissolved nutrients along the course of RE

Nutrients (mg/l)	Upper course	Middle course	Lower course	$\bar{X} \pm SD$
Ca^{2+}	3.93	3.39	2.39	3.24 ±0.78
Mg^{2+}	4.07	3.27	2.32	3.22 ± 0.88
K^{+}	2.51	2.40	2.44	2.45 ± 0.06
Na^{+}	2.49	2.22	2.21	2.31 ± 0.16
NO_3^-	0.33	0.31	0.25	0.30 ± 0.04
HCO_3^-	2.73	2.53	2.82	2.69 ± 0.15
Cl^-	81.35	81.29	72.63	78.42 ± 5.02
SO_4^{2-}	0.31	0.29	0.30	0.30 ± 0.01

ANOVA of the inter-stage variation of the selected dissolved nutrients is presented in Table 12. The analysis reveals that there is no significant variation in the inter-stage concentration of dissolved nutrients in RE. The insignificant statistical variation of inter-stage concentration of dissolved nutrients in the river could be ascribed to largely similar socio-economic activities along the course of the river which as earlier noted include fishing, sand-mining, agriculture, and transportation (Omo-Irabor and Olobaniyi, 2007; Usherhe *et al.*, 2016).

Table 12: ANOVA of dissolved nutrients along the course of RE

Source of variation	SS	df	MS	F	P-value	F crit
Between groups	11.00	2	5.50	0.01	1.00	3.47
Within groups	15372.28	21	732.01			
Total	15383.28	23				

T-statistics of the variations of the concentration of the sampled nutrients between the rainy season and the dry season are presented in Table 13. The analysis shows that the concentrations of the dissolved nutrients investigated in this study did not differ significantly at the upper course, middle course and lower course between the rainy season and dry season.

Table 13: T-test of the difference in dissolved between rainy and dry season

Pairs	Paired differences					*t*	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% confidence interval of the difference				
				Lower	Upper			
Lower course 1 - Lower course 2	-2.03	6.52	2.30	-7.47	3.427	-0.88	7	0.41
Middle course 1- Middle course 2	-1.56	5.11	1.81	-5.83	2.71	-0.86	7	0.42
Upper course 1 - Upper course 2	-0.73	3.35	1.18	-3.53	2.07	-0.62	7	0.56

Where 1 and 2 represents wet season and dry season respectively

4. CONCLUSION

The paper examined the seasonal variations of dissolved nutrients along the course of River Ethiope (RE). The study shows insignificant statistical variations in the concentration of the selected dissolved nutrients at each of the stages and among the stages of RE. Positive significant relationship was observed between Na^+ and K^+, SO_4^{2-} and Na^+ as well as SO_4^{2-} and K^+ at the upper course while positive significant association existed between NO_3^- and Ca^{2+} and Mg^{2+} and between HCO_3^- and Na^+ at the middle course. Similarly, positive significant relationships subsist between Na^+ and K^+, NO_3^- and Ca^{2+}, HCO_3^- and K^+ and Na^+ as well as between SO_4^{2-} and and K^+, Na^+ and HCO_3^- at the lower course. The highest and lowest concentrations of nutrients at the upper course were Cl^- and SO_4^{2-} respectively while the highest and lowest concentrations at the middle course were Cl^- and SO_4^{2-} respectively whereas at the lower course, highest and the lowest concentrations were Cl^- and NO_3^-. The significant relationships between the concentrations of some of the selected nutrients suggest similarity in the natural and anthropogenic sources of nutrients in the catchment area of RE.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

REFERENCES

American Public Health Association (APHA) (1998). *Standard methods for the examination of water and waste water*. 20th edition, Washington

Arnell, N.W., Halliday, S.J., Bartterbee, R.W., Skeffinghton, R. A. and Wade, A.J. (2015). The implications of climate change for the water environment in England. *Progress in Physical Geography*, 39 (1), pp. 93–120.

Barakat, A., El Baghdadi, M., Rais, J., Aghezzaf, B. and Slassi, M. (2016). Assessment of spatial and seasonal water quality variation of Oum Er Rbia River (Morocco) using multivariate statistical techniques. *International soil and water conservation research*, *4*(4), pp. 284-292.

Bogdał, A., Kowalik, T., Ostrowski, K. and Skowron, P. (2016). Seasonal variability of physicochemical parameters of water quality on length of Uszwica River. *Journal of Ecological Engineering*, 17 (1), pp. 161–170.

Cai, Y., Guo, L., Douglas, T. A. and Whitledge T. E. (2008). Seasonal variations in nutrient concentrations and speciation in the Chena River, Alaska. *Journal of Geophysical Research*, 113, G03035,

Doherty, M, Yager, P.L., Moran, M.A., Coles, V.J., Fortunato, C.S, Krusche, A.V., Medeiros, P.M., Payet, J.P, Richey, J.E., Satinsky, B.M., Sawakuchi, H.O., Ward, N.D. and Crump, B.C. (2017). Bacterial biogeography across the Amazon River-Ocean continuum. *Frontiers in Microbiology*, 8, p. 882.

Edwards, A.C., Hooda, P.S. and Cook, Y. (2001). Determination of nitrate in water containing dissolved organic carbon by ultraviolet spectroscopy. *International Journal of Environmental Analytical Chemistry*, 80 (1), pp. 49-59.

EPA (Environmental Protection Agency) (1971). *Method 352.1: nitrogen, nitrate (colorimetric,brucine) by spectrophotometer*. United States Environmental Protection Agency, Available at https://www.epa.gov/sites/production/files/2015-08/documents/method_352-1_1971.pdf. Accessed on 26th Aril, 2020.

Gong Y., Yu Z., Yao Y., Chen H., Mi T. and Tan J. (2015). Seasonal variation and sources of dissolved nutrients in the Yellow River, China. *International Journal of Environmental Research and Public Health*, 12, pp. 9603-9622.

Halliday, S.J., Skeffington, R.A., Bowes, M.J., Gozzard, E., Newman, J.R., Loewenthal, M., Palmer-Felgate, E.J., Jarvie, H.P. and Wade, A.J. (2014). The water quality of the River Enborne, UK: Observations from high-frequency monitoring in a rural, lowland river system. *Water,* 6, pp. 150-180.

Ikomi, R.B., Arimoro, F.O. and Odihirin, O.K. (2005). Composition, distribution and abundance of macroinvertebrates of the upper reaches of River Ethiope, Delta State Nigeria. *Zoologist*, 3, pp. 68-81.

Iloba, K.I. (2017). Rotifers of River Ethiope, Delta State, Nigeria. *International Journal of Fisheries and Aquatic Studies*, 5 (2), pp. 74-79.

Liang, C., Xian, W. and Pauly, D. (2018). Impacts of ocean warming on China's fisheries catches: an application of "mean temperature of the catch" concept. *Frontiers in Marine Science*, *5*, p. 26.

Liu, S.M., Qi, X.H., Li, X., Ye, H.R., Wu, Y., Re,n J.L., Zhang, J. and Xu, W.Y. (2015). Nutrient dynamics from the Changjiang (Yangtze River) estuary to the East China Sea. *Journal of Marine Systems*, *154*, pp. 15-27

Nilsson, C. and Renofalt, B.M. (2008). Linking flow regime and water quality in rivers: a challenge to adaptive catchment management. *Ecology and Society* 13(2), p. 18.

Omo-Irabor, O. O. and Olobaniyi, S. B. (2007). Investigation of the Hydrological Quality of Ethiope River Watershed, Southern Nigeria. *Journal of Applied Sciences and Environmental Management*, 11 (2), pp. 13 - 19

Rahaman, S. M.B., Biswas, S.K., Rahaman, M.D.S., Ghosh, A.K., Sarder, L., Siraj, S.M.S. and Islam, S.S. (2014). Seasonal nutrient distribution in the Rupsha-Passur tidal river system of the Sundarbans mangrove forest, Bangladesh. *Ecological Processes*, 3, p. 18.

Santana, L.M., Moraes, M.E.B., Silva, D.M.L and Ferragui, C. (2016). Spatial and temporal variation of phytoplankton in a tropical eutrophic river. *Brazilian Journal Biology,* 76 (3), pp. 600-610.

Shukla, M. and Arya, S. (2018). Determination of Chloride ion (Cl-) concentration in ganga river water by Mohr method at Kanpur, India. *Green Chemistry & Technology Letters*, *4*(1), pp. 6-8.

Usherhe, O., Origho, T. and Ewhuwhe-Ezo, J. (2016). Determinant of Water Quality and Suitability of River Ethiope for Fish Survival in Southern Nigeria. *Canadian Journal of Agriculture and Crops*, 1(1), pp. 11-18

Wen, L., Jiann, K. and Liu, K. (2008). Seasonal variation and flux of dissolved nutrients in the Danshuei Estuary, Taiwan: A hypoxic subtropical mountain river. *Estuarine, Coastal and Shelf Science*, 78, pp. 694–704.

Yang, H., Shen, Z., Zhang, J. and Wang, W. (2007). Water quality characteristics along the course of the Huangpu River (China). *Journal of Environmental Sciences*, 19, pp. 1193–1198.